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Implications of the recent fluctuations in the growth rate of tropospheric methane

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[1] Global measurements show that the mixing ratio of tropospheric methane (CH_4) increased by 1.1% (19.5 ± 1.7 ppbv) over the five-year period 1996–2000, with striking fluctuations in its annual growth rate. Whereas the global CH_4 growth rate reached 15.9 ± 0.7 ppbv yr^{-1} in 1998, the growth rate was -2.1 ± 0.8 ppbv yr^{-1} in 2000. This is the first time in our 23-year global monitoring program that we have measured a negative annual CH_4 growth rate. The CH_4 growth rate fluctuates in an unpredictable fashion, and we reemphasize that global CH_4 concentrations cannot be extrapolated into the future based on past trends. As a result, we suggest that the slowing of the CH_4 growth rate during much of the 1980s and 1990s cannot be used to imply that CH_4 will no longer be of concern in greenhouse gas studies during this century.

INDEX TERMS: 0325 Atmospheric Composition and Structure: Evolution of the atmosphere; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 1610 Global Change: Atmosphere (0315, 0325)

1. Introduction

[2] Methane (CH_4) plays critical roles in the chemistry and radiative balance of the atmosphere [Levy, 1971; Blake and Rowland, 1988; Schimel *et al.*, 1996; Seinfeld, 1999]. The mixing ratio of atmospheric CH_4 varied between 350–750 ppbv from 110,000 to 300 years ago [Rasmussen and Khalil, 1984; Brook *et al.*, 1996]. Ice core samples have shown that the CH_4 growth rate increased with the onset of the Industrial Revolution, to a level of 14 parts per billion by volume per year (ppbv yr^{-1}) by the 1970s [Etheridge *et al.*, 1992]. The sources of the CH_4 increase include energy use, rice paddies, domestic ruminants, biomass burning, and landfills [Rasmussen and Khalil, 1984].

[3] The first extensive measurements of the global distribution of atmospheric CH_4 were made in 1978 [Blake *et al.*, 1982], and additional global monitoring networks were established in the early 1980s [Steele *et al.*, 1987; Prinn *et al.*, 2000]. Between 1978 and 1987 our group reported an 11% increase in the global tropospheric CH_4 mixing ratio, at an average annual increase of 16 ± 1 ppbv yr^{-1} [Blake and Rowland, 1988]. The concentration of atmospheric CH_4 continued to increase with significant interannual variability, but the growth rate slowed in the 1980s [Steele *et al.*, 1992; Khalil and Rasmussen, 1993] and continued to decline into the 1990s [Dlugokencky *et al.*, 1994a; 1998].

[4] Based on measurements from 1984–96 and assuming constant global hydroxyl radical (OH) concentration, it has been suggested that the decreasing growth rate in atmospheric CH_4 reflects the approach to a steady state, on a timescale comparable to methane's atmospheric lifetime [Dlugokencky *et al.*, 1998]. The

lifetime of atmospheric CH_4 is about 8 years [Lelieveld *et al.*, 1998; Karlsdóttir and Isaksen, 2000], and some groups have interpreted the results in Dlugokencky *et al.* [1998] to mean that increasing CH_4 will no longer be of concern in greenhouse gas studies. Here we present recent changes in the CH_4 growth rate that show that the global concentration of CH_4 has varied in an unpredictable fashion, and we suggest that it is premature to believe that CH_4 increases will no longer be of concern in greenhouse gas studies during this century.

2. Experimental

[5] Our group has monitored the mixing ratio of tropospheric CH_4 at remote locations in the Pacific Basin since 1978 [Blake *et al.*, 1982; Mayer *et al.*, 1982; Blake and Rowland, 1986; 1988]. Each season (usually in March, June, September and December), approximately 60–80 whole air samples are collected over a 3-week period in 40–45 locations. The sampling network covers as much of the Earth's latitudinal range as is feasible for us (currently 71°N to 47°S). Individual air samples are collected at sites that our experience has shown to yield remote concentrations, typically along the coast when the prevailing wind is from the ocean. The air samples are collected in conditioned, evacuated 2-L stainless steel canisters each equipped with a stainless steel bellows valve. During sampling the canister is filled to ambient pressure over a period of about one minute. At the end of the collection period the sampling canisters are returned to our laboratory for analysis.

[6] The CH_4 mixing ratio within each sample is determined by gas chromatography (HP-5890A) with flame ionization detection. The use of primary calibration standards dating back to late 1977 ensures that our measurements are internally consistent. The CH_4 mixing ratios are reported for dry air, and are made relative to a primary standard purchased from the Matheson Gas Company in 1977 and to a National Bureau of Standards (NBS) standard purchased in August, 1982. The uncertainty in the NBS standard is $\pm 1\%$. Our analytical precision is determined by alternating measurements of secondary standards with aliquots from an individual air sample. Our analytical precision was 3 ppbv in the 1980s and is currently better than 2 ppbv. Data points are individually inspected, and points that do not represent remote values are removed (usually 2–5 samples per seasonal collection).

[7] The CH_4 mixing ratios presented here were obtained between January 1978 and June 2001, and the annual growth rates use data collected between April 1983 and December 2000 (data before 1983 have not been included in the growth rate analysis because the CH_4 surveys were conducted less frequently than once a season). Methane is long-lived relative to our sampling frequency, and our temporal and spatial resolution is suitable for monitoring the globally averaged growth or decline of CH_4 .

[8] The global CH_4 source strength is roughly 3 times larger in the Northern Hemisphere (NH) than in the Southern Hemisphere (SH) [Fung *et al.*, 1991; Houweling *et al.*, 1999]. As a result, CH_4

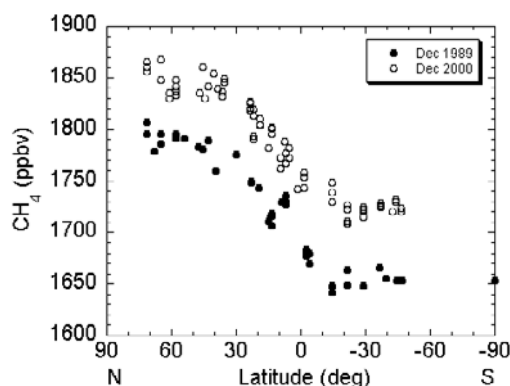


Figure 1. Tropospheric CH_4 mixing ratios (ppbv) for individual air samples collected in December 1989 and December 2000. The South Pole sample (-90° latitude) shows that CH_4 is well-mixed throughout the Southern Hemisphere.

mixing ratios show a characteristic north-south gradient, with higher mixing ratios in the NH than in the SH (Figure 1). Globally averaged CH_4 mixing ratios are determined using an equal surface area weighting method, whereby the Earth is separated into a designated number of latitudinal bands or 'boxes', with each box containing approximately equal masses of tropospheric air. The technique is used to avoid over-weighting the global CH_4 average towards more accessible sampling areas. We have found that choosing 16 boxes offers the best balance between displaying mixing ratio changes with latitude, and retaining a sufficient number of samples per box. The latitudinal boundaries that separate the Earth into 16 equal surface areas lie at the equator and at $7.2, 14.5, 22.0, 30.0, 38.7, 48.6$ and 61.0° in each hemisphere. Boxes with no data are assigned appropriate values and errors based on the data from neighbouring boxes. The global average CH_4 mixing ratio for a given season is the arithmetic mean of the 16 box averages. The uncertainty in the average CH_4 mixing ratio for each box is the standard deviation of the mean value (the standard error). The uncertainty in the seasonal average is the sum of the standard errors for each box, added in quadrature, divided by the number of boxes.

3. Results and Discussion

[9] The globally averaged CH_4 mixing ratios show a seasonal cycle superimposed upon a longer-term increase (Figure 2). The long-term increase in the CH_4 mixing ratio (MR_{CH_4}) can be described by a second order polynomial fit:

$$MR_{\text{CH}_4} = k_0 + k_1 \times \text{year} + k_2 \times \text{year}^2 \quad (1)$$

where k_0 , k_1 and k_2 are constants (for the data collected between January 1978 and June 2001, $k_0 = -1,766,702$, $k_1 = 1766.723$, and $k_2 = -0.441,245$, with $r^2 = 0.991$). Previous studies have also found that the long-term trend in the CH_4 mixing ratio is well-described by a polynomial fit [Dlugokencky et al., 1994b, 1998]. When fitting the data with a polynomial curve it is important to be aware of the implicit, incorrect assumption that all of the factors affecting the CH_4 mixing ratio vary smoothly over time, with no abrupt discontinuities. We have fitted the data in Figure 2 with an interpolated curve (a curve that passes through the data points and matches the slopes at those points) rather than a polynomial fit, to emphasize the possibility of a discontinuous change in some factor affecting the CH_4 balance. For example, the sudden eruption of Mt. Pinatubo in 1991 likely contributed to the sharp increase in the CH_4 growth rate shortly thereafter [Dlugokencky et al., 1996], while the growth rate decrease in the NH in 1992

has been attributed to decreased emissions from northern wetlands [Hogan and Harriss, 1994], increased photochemical removal of CH_4 [Bekki et al., 1994], and the effect of the collapse of the Soviet Union on natural gas production [Dlugokencky et al., 1994a]. A second implicit assumption associated with fitting a polynomial curve to the data is that the trend can be extrapolated into the future, whereas it has been noted that future CH_4 mixing ratios cannot be extrapolated from past trends [Khalil and Rasmussen, 1993; see below].

[10] Annual CH_4 mixing ratios were calculated using the average of the 4 seasonal means in a given year. Annual growth rates were then calculated as the slope of two consecutive annual global CH_4 mixing ratios, using the data set from 1983–2000 inclusive (Figures 3a and 3b). The uncertainty in the annual CH_4 mixing ratio is given by the sum of the standard errors of the seasonal means for that year, added in quadrature, divided by the number of seasonal means. The uncertainty in individual growth rate points is given by the sum of the uncertainties of the two annual CH_4 mixing ratios from which the growth rate was derived, added in quadrature.

[11] The average CH_4 growth rate for the 18-year period 1983–2000, given by the arithmetic mean of the 17 calculated growth rate points, was $8.5 \pm 0.2 \text{ ppbv yr}^{-1}$. Over the same period, the average rate at which the CH_4 growth rate changed (ppbv/yr/yr) was $-0.6 \pm 0.3 \text{ ppbv yr}^{-2}$. Within the past few years, the CH_4 growth rate has displayed notable, unpredictable fluctuations (Figures 3b and 3c). The annual CH_4 growth rate reached $15.9 \pm 0.7 \text{ ppbv yr}^{-1}$ in 1998, and similarly high growth rates have not been measured since the eruption of Mt. Pinatubo in 1991 (Figure 3b). The change in the CH_4 growth rate was $14.2 \pm 1.1 \text{ ppbv yr}^{-2}$ over the period 1997–98, and it is the largest growth rate increase we have recorded over a comparable time period since we began our global monitoring program (Figure 3c). The CH_4 mixing ratio continued to increase in 1999, though at a much slower rate of $2.8 \pm 0.7 \text{ ppbv yr}^{-1}$. The growth rate change over the period 1998–99 was $-13.1 \pm 1.0 \text{ ppbv yr}^{-2}$, and it is the largest growth rate decrease we have recorded during our 23-year global monitoring program. In 2000, the global growth rate of CH_4 was $-2.1 \pm 0.8 \text{ ppbv yr}^{-1}$. This is the first time in our monitoring program that we have measured a negative annual CH_4 growth rate.

[12] The magnitudes and locations of the growth rate peaks and troughs show good agreement with published data (which are available until the end of 1999; Dlugokencky et al. [1998, 2001]), given that the two global monitoring networks use different sampling strategies and data analysis procedures. For example, our data do not show the instantaneous negative growth rate in 1992 because a direct interpolation was used here whereas Dlugokencky et al. [1998] used a different curve fitting technique.

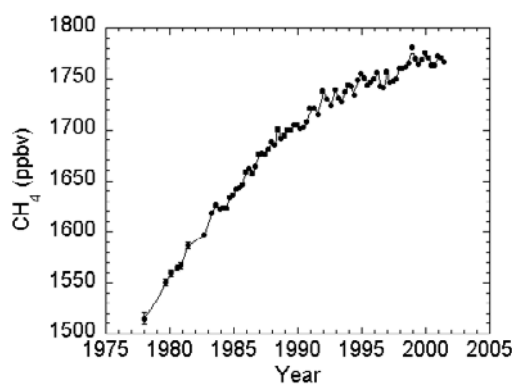


Figure 2. Seasonally averaged global CH_4 mixing ratios (ppbv) for January 1978–June 2001. The solid line is an interpolated curve fit to the data points.

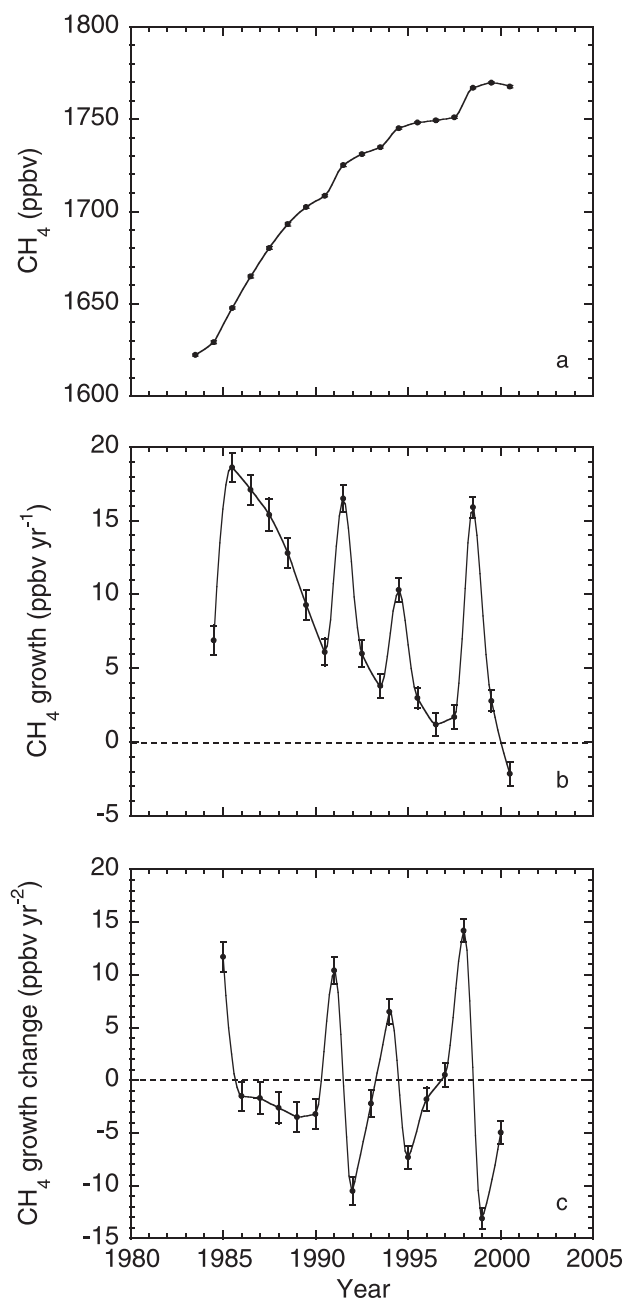


Figure 3. Annual global tropospheric CH₄ (a) mixing ratio (ppbv), (b) growth rate (ppbv yr⁻¹), and (c) growth rate change (ppbv yr⁻²), for 1983–2000. The solid line in each panel is an interpolated curve fit to the data points.

[13] Some groups have understood the decreasing CH₄ growth rate during much of the 1980s and 1990s to mean that CH₄ increases will no longer be of concern in greenhouse gas studies (Section 1). By contrast, we emphasize that it is premature to believe that the CH₄ burden is ceasing to increase. First, the global burden of CH₄ increased by 1.1% (19.5 ± 1.7 ppbv) between 1996–2000, and, in the five years since 1996, the CH₄ burden has not followed a pattern that is in keeping with the approach to a steady state on a timescale comparable to its atmospheric lifetime (Figure 3a). Second, the strikingly high CH₄ growth rate in 1998, followed by our first recorded negative CH₄ growth rate in 2000, highlight the unpredictable nature of changes in methane's tropospheric concentration (Figure 3b).

[14] The increase in the tropospheric CH₄ burden between 1996–2000 was driven primarily by the large CH₄ growth in 1998 (Figure 3a). Similarly, the increase in the global CH₄ burden between 1991–2000 (3.4%, or 59.1 ± 2.5 ppbv) was driven by three years of notably high growth, in 1991, 1994 and 1998. The three years of high growth caused the CH₄ burden to increase in a series of steps during the 1990s, in contrast to a smoother increase during the 1980s (Figure 3a). Although the pattern of CH₄ growth was different during the 1990s than the 1980s, we caution against viewing each year of high CH₄ growth as an anomaly against a trend of declining CH₄ growth. In particular, it has been suggested that increased CH₄ emissions from wetlands, because of a warmer and wetter environment in wetland regions, may have contributed to the high CH₄ growth in 1998 [Dlugokencky et al., 2001]. If temperate and tropical wetlands continue to encounter warm, wet conditions during certain years, then it would not be surprising to observe more years of high CH₄ growth in the future.

[15] During the past century the sources of CH₄ increase were related to agriculture and were closely tied to population increase, whereas it has been suggested that new CH₄ sources are not closely related to population growth [Khalil and Rasmussen, 1993]. We reemphasize that the decoupling of the sources of past increases from the sources of present and future increases makes attempting to predict future CH₄ mixing ratios based on past changes questionable. In addition, discontinuous events that may affect the CH₄ balance (such as volcanic eruptions) can occur without warning and with unpredictable effects. El Niño and La Niña events, the frequency and severity of which could be affected by climate change, might also play a role in the fluctuations of CH₄. Hansen et al. [2000] have proposed that CH₄ emissions be reduced by 30% over the next 50 years. The possibility of legislation to control CH₄ emissions, which we encourage, further impedes our ability to predict future CH₄ burdens.

[16] In addition to changing and discontinuous CH₄ sources, variations in OH concentration can also cause significant variations in the CH₄ growth rate [Dlugokencky et al., 1996]. For example, the decrease in steady-state OH following the eruption of Mt. Pinatubo is believed to have led to the large CH₄ growth rates during 1991 and early 1992 [Dlugokencky et al., 1996]. The possibility of a trend in global OH concentration during the past two decades has been addressed in a number of recent measurement and modeling studies [Prinn et al., 1995, 2001; Krol et al., 1998; Karlsdóttir and Isaksen, 2000]. Karlsdóttir and Isaksen [2000] used a 3-D model to suggest that over the period 1980–96 the average global OH concentration increased by $0.43\% \text{ yr}^{-1}$, the lifetime of CH₄ decreased by $0.49\% \text{ yr}^{-1}$, and annual average CH₄ emissions increased by $0.67\% \text{ yr}^{-1}$. Prinn et al. [2001] used methyl chloroform measurements to suggest that global average OH levels rose $15 \pm 22\%$ between 1979–89, then decreased to levels in 2000 that were about $10 \pm 24\%$ below 1979 values. Their estimated OH trends imply a time-varying lifetime for CH₄ that decreased up until 1988 and has subsequently increased. A continuing negative trend in OH could contribute to relatively higher CH₄ growth.

[17] Because the trends in CH₄ sources and sinks are changing and unpredictable, upcoming variations in the global CH₄ concentration cannot be estimated in advance. Some recent modeling studies have cited the analysis in Dlugokencky et al. [1998] to suggest that CH₄ levels may not grow much above current levels [Kirk-Davidoff et al., 1999] and in simulating a stabilizing CH₄ source [Lassey et al., 2000]. By contrast, the Intergovernmental Panel on Climate Change (IPCC) Special Report on Emissions Scenarios features a wide range of global CH₄ emission scenarios, some of which have large CH₄ growth rates throughout the 21st century [Nakicenovic et al., 2001]. Given that future CH₄ concentrations are currently unpredictable, it is important to continue to allow for changes in the global CH₄ concentration, and not assume that CH₄ concentrations will cease to grow much above current levels.

4. Conclusions

[18] Global measurements show that the mixing ratio of tropospheric CH₄ increased by 1.1% (19.5 ± 1.7 ppbv) between 1996–2000, with striking fluctuations in its annual growth rate. The growth rate of CH₄ in 1998 (15.9 ± 0.7 ppbv yr⁻¹) has not been as high since the eruption of Mt. Pinatubo in 1991, and the increase in the CH₄ growth rate for 1997–98 (14.2 ± 1.1 ppbv yr⁻²) is the largest we have measured in our 23-year record. In 2000, we measured a negative CH₄ growth rate (-2.1 ± 0.8 ppbv yr⁻¹) for the first time in our global monitoring program.

[19] The striking fluctuations in the CH₄ growth rate during the past few years highlight the unpredictable nature of changes in the global CH₄ burden, and provide excellent opportunities for us to test our understanding of the processes that control CH₄ emission to and removal from the atmosphere. The trend in CH₄ growth was more variable during the 1990s than during the 1980s, and the high CH₄ growth rate in 1998, followed by negative CH₄ growth in 2000, suggests that a change of some sort might be underway. Because the sources of the variations in the CH₄ burden are changing and discontinuous, future CH₄ concentrations cannot be predicted based on past growth rate trends. Warm, wet conditions in wetland environments and a continuing negative trend in global OH concentration are among the events that could contribute to an increase in the global CH₄ burden. By contrast, an increase in OH concentration or legislation to control anthropogenic CH₄ emissions could contribute to lower or negative CH₄ growth.

[20] Changes in the CH₄ burden this century may follow any one of a wide range of scenarios, and we suggest that the slowing of the CH₄ growth rate during much of the 1980s and 1990s cannot be used to indicate that CH₄ will no longer be of concern in greenhouse gas studies. Should the concentration of CH₄ level off, there is still the possibility of it subsequently increasing or decreasing from that point. As a result, greenhouse gas modeling studies need to continue to allow for changes in the global CH₄ concentration. Because CH₄ is relatively short-lived compared to carbon dioxide (CO₂), reduction of CH₄ emissions will be quickly reflected in the atmosphere. A reduction of CH₄ concentration could be an important short-term offset to the considered growth in CO₂, and efforts to control CH₄ are strongly encouraged.

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References

- Bekki, S., K. A. Law, and J. A. Pyle, Effect of ozone depletion on atmospheric CH₄ and CO, *Nature*, 371, 595–597, 1994.
- Blake, D. R., et al., Global increase in atmospheric methane concentrations between 1978 and 1980, *Geophys. Res. Lett.*, 9, 477–480, 1982.
- Blake, D. R., and F. S. Rowland, World-wide increase in tropospheric methane, 1978–1983, *J. Atmos. Chem.*, 4, 43–62, 1986.
- Blake, D. R., and F. S. Rowland, Continuing world-wide increase in tropospheric methane, 1978–1987, *Science*, 239, 1129–1131, 1988.
- Brook, E. J., T. Sowers, and J. Orchado, Rapid variations in atmospheric methane concentration during the past 110,000 years, *Science*, 273, 1087–1091, 1996.
- Dlugokencky, E. J., K. A. Masarie, P. M. Lang, P. P. Tans, L. P. Steele, and E. G. Nisbet, A dramatic decrease in the growth rate of atmospheric methane in the northern hemisphere during 1992, *Geophys. Res. Lett.*, 21, 45–48, 1994a.
- Dlugokencky, E. J., L. P. Steele, P. M. Lang, and K. A. Masarie, The growth rate and distribution of atmospheric methane, *J. Geophys. Res.*, 99, 17,021–17,043, 1994b.
- Dlugokencky, E. J., E. G. Dutton, P. C. Novelli, P. P. Tans, K. A. Masarie, K. O. Lantz, and S. Madronich, Changes in CH₄ and CO growth rates after the eruption of Mt. Pinatubo and their link with changes in tropical tropospheric UV flux, *Geophys. Res. Lett.*, 23, 2761–2764, 1996.
- Dlugokencky, E. J., K. A. Masarie, P. M. Lang, and P. P. Tans, Continuing decline in the growth rate of the atmospheric methane burden, *Nature*, 393, 447–450, 1998.
- Dlugokencky, E. J., B. P. Walter, K. A. Masarie, P. M. Lang, and E. S. Kasischeke, Measurements of an anomalous global methane increase during 1998, *Geophys. Res. Lett.*, 28, 499–502, 2001.
- Etheridge, D. M., G. I. Pearman, and P. J. Fraser, Changes in tropospheric methane between 1841 and 1978 from a high accumulation-rate Antarctic ice core, *Tellus*, 44B, 282–294, 1992.
- Fung, I., J. John, J. Lerner, E. Matthews, M. Prather, L. P. Steele, and P. J. Fraser, Three-dimensional model synthesis of the global methane cycle, *J. Geophys. Res.*, 96, 13,033–13,065, 1991.
- Hansen, J., M. Sato, R. Ruedy, A. Lacis, and V. Oinas, Global warming in the twenty-first century: An alternative scenario, *Proc. Natl. Acad. Sci.*, 97, 9875–9880, 2000.
- Hogan, K. B., and R. C. Harriss, Comment on ‘A dramatic decrease in the growth rate of atmospheric methane in the northern hemisphere during 1992’ by E. J. Dlugokencky et al., *Geophys. Res. Lett.*, 2445–2446, 1994.
- Houweling, S., T. Kaminski, F. Dentener, J. Lelieveld, and M. Heimann, Inverse modeling of methane sources and sinks using the adjoint of a global transport model, *J. Geophys. Res.*, 104, 26,137–26,160, 1999.
- Karlsdóttir, S., and I. S. A. Isaksen, Changing methane lifetime: Possible cause for reduced growth, *Geophys. Res. Lett.*, 27, 93–96, 2000.
- Khalil, M. A. K., and R. A. Rasmussen, Decreasing trend of methane: Unpredictability of future concentrations, *Chemosphere*, 26, 803–814, 1993.
- Kirk-Davidoff, D. B., E. J. Hintsa, J. G. Anderson, and D. W. Keith, The effect of climate change on ozone depletion through changes in stratospheric water vapour, *Nature*, 402, 399–401, 1999.
- Lassey, K. R., D. C. Lowe, and M. R. Manning, The trend in atmospheric methane $\delta^{13}\text{C}$ and implications for constraints on the global methane budget, *Global Biogeochem. Cycles*, 14, 41–49, 2000.
- Lelieveld, J., P. J. Crutzen, and F. J. Dentener, Changing methane lifetime: Possible cause for reduced growth, *Tellus*, 50B, 128–150, 1998.
- Levy, H., Normal atmosphere: large radical and formaldehyde concentrations predicted, *Science*, 173, 141–143, 1971.
- Mayer, E. W., D. R. Blake, S. C. Tyler, Y. Makide, D. C. Montague, and F. S. Rowland, Methane: Interhemispheric concentration gradient and atmospheric residence time, *Proc. Natl. Acad. Sci.*, 79, 1366–1370, 1982.
- Nakicenovic, N., et al., Intergovernmental Panel on Climate Change (IPCC), Special Report on Emissions Scenarios, <http://www.grida.no/climate/ipcc/emission/index.htm>, 2001.
- Prinn, R. G., R. F. Weiss, B. R. Miller, J. Huang, F. N. Alyea, D. M. Cunnold, P. J. Fraser, D. E. Hartley, and P. G. Simmonds, Atmospheric trends and lifetime of CH₃CCl₃ and global OH concentrations, *Science*, 269, 187–192, 1995.
- Prinn, R. G., R. F. Weiss, P. J. Fraser, P. G. Simmonds, et al., A history of chemically and radiatively important gases in air deduced from ALE/GAGE/AGAGE, *J. Geophys. Res.*, 105, 17,751–17,792, 2000.
- Prinn, R. G., J. Huang, R. F. Weiss, D. M. Cunnold, P. J. Fraser, P. G. Simmonds, A. McCulloch, C. Harth, P. Salameh, S. O’Doherty, R. H. J. Wang, L. Porter, and B. R. Miller, Evidence for substantial variations of atmospheric hydroxyl radicals in the past two decades, www.scienceexpress.org, 10.1126/science.1058673, 2001.
- Rasmussen, R. A., and M. A. K. Khalil, Atmospheric methane in recent and ancient atmospheres: concentrations, trends, and interhemispheric gradient, *J. Geophys. Res.*, 89, 11,599–11,605, 1984.
- Schimel, D., et al., in *Climate Change 1995: The Science of Climate Change*, Edited by J. T. Houghton, L. G. Meira Filho, B. A. Callander, N. Harris, A. Kattenberg, and K. Maskell, Eds., pp. 65–131, Cambridge University Press, Cambridge, 1996.
- Seinfeld, J. H., in *Reactive Hydrocarbons in the Atmosphere*, Edited by C. N. Hewitt, pp. 293–319, Academic Press, San Diego, 1999.
- Steele, L. P., P. J. Fraser, R. A. Rasmussen, M. A. K. Khalil, T. J. Conway, A. J. Crawford, R. H. Gammon, K. A. Masarie, and K. W. Thoning, The global distribution of methane in the troposphere, *J. Atmos. Chem.*, 5, 125–171, 1987.
- Steele, L. P., E. J. Dlugokencky, P. M. Lang, P. P. Tans, R. C. Martin, and K. A. Masarie, Slowing down of the global accumulation of atmospheric methane during the 1980s, *Nature*, 358, 313–316, 1992.

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